



In situ photodeposition of NiO_x on CdS for hydrogen production under visible light: Enhanced activity by controlling solution environment



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ABSTRACT

Low-cost and effective cocatalysts nickel oxides were deposited on CdS via a simple in situ photodeposition under different solution. It was found that the environment of photodeposition played a critical role in photocatalytic H₂ evolution activities. CdS loaded nickel oxide in alkaline solution showed the highest activity of photocatalytic hydrogen production, reaching to 590.8 μmol h⁻¹ when the mole ratio of Ni²⁺ and CdS was 0.01, which was 117 times higher than that of pure CdS. The high photocatalytic hydrogen production activity might be attributed to the following reasons: (1) NiO could disperse on CdS tightly; (2) the OH⁻ in the alkaline solution could be benefit for the transfer of holes. Thus, the holes and electrons could be separated efficiently.

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1. Introduction

H₂ production from photocatalytic water splitting using semiconductor photocatalysts have been studied as a potential means of clean, large-scale fuel production for solving energy and environmental problems. Countless research efforts have been devoted to the development of efficient semiconductor photocatalysts for water splitting [1–3]. CdS photocatalyst has been extensively explored for photocatalytic hydrogen production because its band gap (2.4 eV) matches well with the spectrum of sunlight and the conduction band edge is much more negative than the H⁺/H₂ reduction potential [4,5]. However, CdS shows low hydrogen production activity because of the rapid recombination of excited electrons and holes, and the fast backward reaction between hydrogen and oxygen [3,6]. Much higher activity for hydrogen production can be obtained after the loading of some noble metal cocatalysts such as Pt, Au, Rh, RuO₂, etc. [7–11], owing to an improved charge-carrier separation efficiency. Aside from noble metals, in recent years, some less expensive transition metal sulfides were also developed as cocatalysts, such as MoS₂, NiS, CuS, WS₂ [12–15].

Nickel and its oxides have been proved as low-cost and efficient cocatalysts for photocatalysis [16,17]. However, it often needs

to be heat treated for their loading process, which is harmful for metal sulfide catalysts because they are not stable during heat treated process. In our previous work [18], the nickel oxides and CdS composite were prepared via a simple in situ photodeposition. The activities of them were even higher than the CdS loaded with noble metal Pt. Further investigations show that the environment of photodeposition plays an important role in the activities of CdS loaded with nickel oxides via in situ photodeposition. In this work, it was found that the environment of photodeposition had great influence on the deposition of nickel oxides and transfer of holes, which resulted in great different photocatalytic hydrogen evolution activity.

2. Experimental

2.1. Preparation of CdS

All of the reagents used were of analytical purity and used without further purification. CdS was synthesized according to the previously reported method [18]. 200 ml Na₂S (0.14 M) solution was added to stirred 250 ml Cd(CH₃COO)₂ (0.14 M) solution, continuously stirred for 24 h, it was filtrated and washed with deionized water several times. Then, it was transferred into a 200-ml stainless Teflon-lined autoclave. The autoclave was sealed and heated at 200 °C for 24 h and then cooled down to room temperature naturally. The resulting precipitates were filtrated and washed using deionized water several times, followed by drying for 12 h at 80 °C.

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2.2. Characterization of catalysts

The crystal structure of the photocatalytic materials was confirmed by X-ray diffraction (Rigaku D/max-2200/PC Japan) with Cu K α (40 kV, 20 mA). The UV–vis diffuse reflection spectra (DRS) were determined by a UV–vis spectrophotometer UV-2450 (Shimadzu, Japan) and were converted to absorbance by the Kubelka–Munk method. The transmission electron microscopy (TEM) measurements were conducted using a JEM-2100F (Japan). The surface area of the samples was determined by BET measurement (Quanta Chrome NOVA1000, USA). The surface electronic state was analyzed by X-ray photoelectron spectroscopy (XPS, Shimadzu-Kratos, Axis Ultra^{DLD}, Japan). All the binding energy (BE) values were calibrated by using the standard BE value of contaminant carbon (C1s = 284.6 eV) as a reference. The content of metal elements were determined by inductively coupled plasma analyzer (ICAP 6000 Radial, Thermo).

2.3. In situ photodeposition and photocatalytic reaction under different solution

The photocatalytic reactions were carried out in a Pyrex reaction cell connected to a closed gas circulation and evacuation system. 0.1 g CdS was suspended in 100 ml of aqueous solution containing 30 ml methanol and certain nickel acetate solution. HCl solution was used to adjust the pH of the solution to 3–4 and 0.5 g NaOH was added to the solution, respectively. The samples loaded with nickels via in situ photodeposition added with HCl, nothing, NaOH were denoted as a-Ni–CdS, b-Ni–CdS, c-Ni–CdS, respectively (the mole ratio of Ni²⁺ in the solution and Cd was 0.05). The suspension was then thoroughly degassed and irradiated by a Xe lamp (300 W) equipped with an optical cutoff filter ($\lambda > 400$ nm, containing 1 M NaNO₂). The amount of H₂ was analyzed using an online gas chromatography.

The apparent quantum efficiency (QE) was measured under the photocatalytic reaction condition with irradiation light at 400 nm by using combined band-pass (Kenko) and cut-off filters (HOYA) and 500 W Xe lamp. The QE was calculated as following equations:

$$\begin{aligned} \text{QE}[\%] &= \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100 \\ &= \frac{\text{number of evolved H}_2 \text{ molecules} \times 2}{\text{number of incident photons}} \times 100 \end{aligned} \quad (1)$$

3. Results and discussion

3.1. Characterization of catalysts samples

As shown in Fig. 1, the absorption intensity of CdS starts to rapid increase at 520 nm, indicating a band gap of 2.4 eV. There is no obvious change on the absorption edges after nickel oxides coating via in situ photodeposition, which indicates that nickel oxides are just deposited on the surface instead of being incorporated into the lattice of CdS. The spectrum for samples loaded with nickel oxides via in situ photodeposition exhibit enhanced absorption among the 540–800 nm by different degrees, which is ascribed to color changes during photocatalytic hydrogen evolution process. From Fig. 1 (inset), it can be seen clearly that the absorption region of 540–800 nm for b-Ni–CdS increases most. However, there is little change about a-Ni–CdS compared with CdS. This is because that different speciation and content of nickel oxides are deposited on the surface of CdS under different environment via in situ photodeposition, which will be further identified in following sections.

The XRD profile of CdS displayed in Fig. 2 can be readily indexed as the (100), (002), (101), (110), (103) and (112) plane of the hexagonal phase of the wurtzite CdS structure, which are well

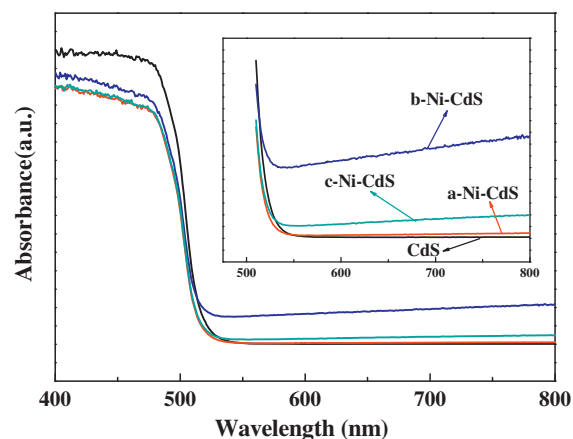


Fig. 1. UV–vis diffuse reflection spectra and magnified image (inset) of CdS, a-Ni–CdS, b-Ni–CdS and c-Ni–CdS.

matched with the standard values according to the main diffraction peaks at 24.9°, 26.6°, 28.4°, 43.7°, 48.1° and 52.0° [18]. After in situ photodeposition for 5 h under different solution, the peaks position of CdS changed little, which indicated that nickel or/and nickel oxides were just deposited on the surface instead of being inserted in the lattice of CdS. No peaks of nickel or nickel oxides were observed. This might be due to their high dispersion and low content on CdS photocatalysts.

XPS is used to identify the valence state of nickels deposited on CdS via in situ photodeposition under different solution. The high-resolution XPS spectra of Ni 2p of the samples are as shown in Fig. 3. There was no signal of nickel when photocatalytic environment was acidic, indicating that there was very little nickel or/and nickel oxides deposited on CdS. When the photodeposition solution was neutral, the Ni 2p_{3/2} peak located at 855.8 eV, suggesting that nickel oxides deposited on CdS are Ni₂O₃ [18,19]. The observed binding energy of Ni 2p_{3/2} shifted to 854.5 eV, which was an indication of the formation of NiO [20,21], when NaOH was added in the photodeposition solution. However, there was no Ni 2p_{3/2} peak at 855.9 eV, indicating that there was no Ni(OH)₂ deposited on CdS after photodeposition for 5 h in alkaline solution [5].

The presence of nickel oxides on the surface of CdS was confirmed by TEM. As shown in Fig. 4, the lattice spacing (0.332 nm) was observed in all samples, corresponding to the (111) plane of the cubic CdS phase [22]. No lattice structure of nickel or nickel oxides was found except some lattice structure defects of CdS after photodeposition in acid solution (Fig. 4A). And nickels or nickel

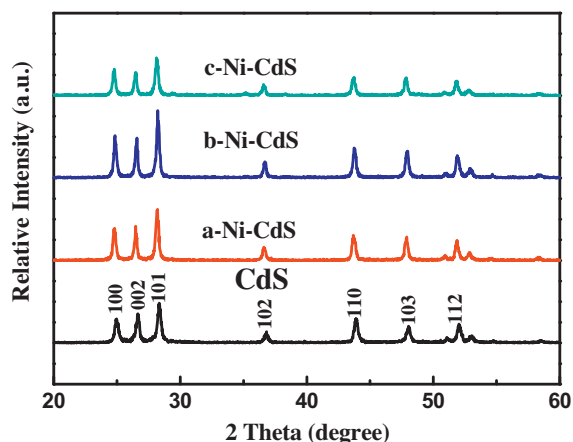


Fig. 2. XRD patterns of CdS, a-Ni–CdS, b-Ni–CdS and c-Ni–CdS.

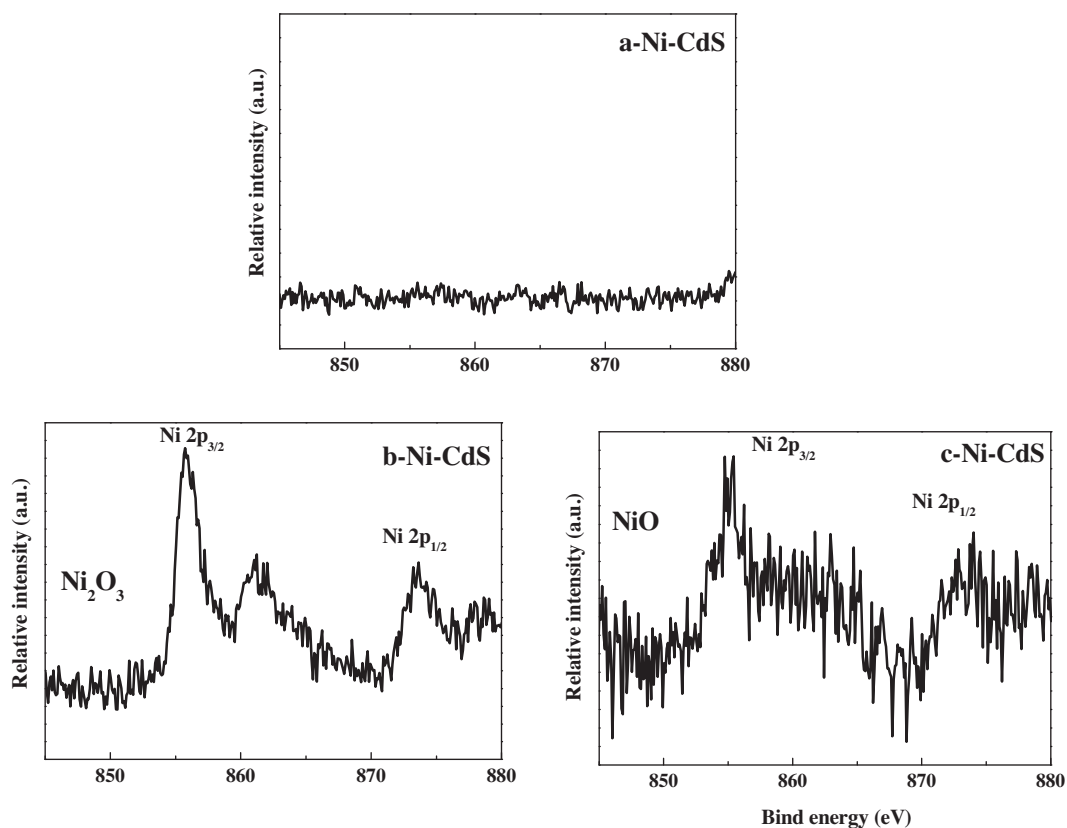


Fig. 3. High-resolution XPS spectra of Ni 2p of a-Ni-CdS, b-Ni-CdS and c-Ni-CdS.

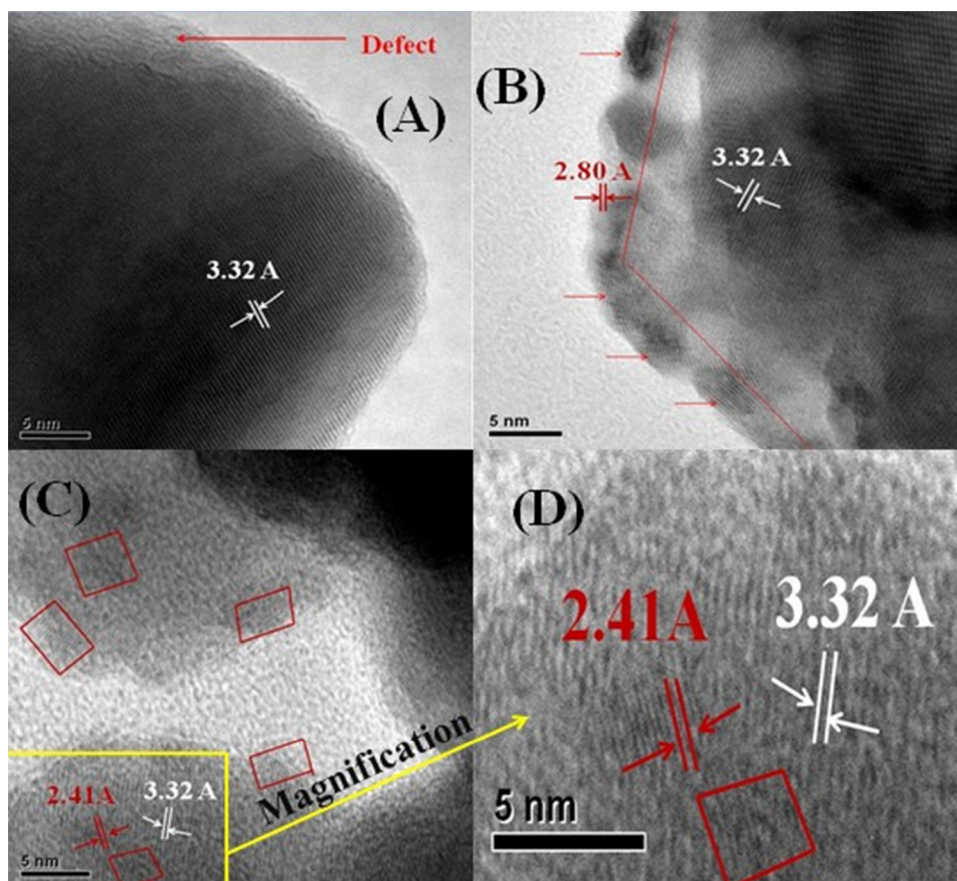


Fig. 4. TEM of (A) a-Ni-CdS, (B) b-Ni-CdS, (C) c-Ni-CdS, (D) the magnified image of graph (C).

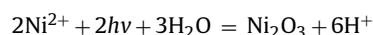
Table 1Nickel contents and pore structure changes of a-Ni-CdS, b-Ni-CdS and c-Ni-CdS after photocatalytic H₂ production for 5 h compared with CdS.

	Samples			
	CdS	a-Ni-CdS [§]	b-Ni-CdS [§]	c-Ni-CdS [§]
Ni/Cd (mol%) ICP-AES	/	Lower than the detection limits	4.95	2.75
Ni/Cd (mol%) EDS	/	Lower than the detection limits	3.05	1.23
S _{BET} (m ² g ⁻¹)	19.0	22.3	18.6	19.2
Pore volume (cm ³ g ⁻¹)	0.203	0.163	0.190	0.176

[§] 0.1 g photocatalysts was irradiated under xenon lamp (300 W) in the aqueous methanol solution (30 vol%) for 5 h.

oxides also could not be detected from the samples photodeposited in acid solution by XPS (Fig. 2), EDS and ICP (as shown in Table 1). The defects might be caused by HCl, which could react with CdS to H₂S and CdCl₂. The pore structure of CdS also changed apparently as shown in Table 1 that pore volume decreased and BET surface area increased, which might caused by pore-collapse. When photodeposition took place in neutral solution, the lattice spacing (0.280 nm) was observed as shown in Fig. 4B, corresponding to the (0 0 2) plane of the face-centered cubic Ni₂O₃ phase, which deposited and gathered on the surface of CdS particles. Similar results had also been found to our previous work [18]. The lattice fringes showed the imaging characteristics of the cubic NiO crystal (Fig. 4D), in which the *d*-spacing of 0.24 nm corresponds to the distance of the (1 1 1) plane [23], when NaOH was added in the photodeposition solution. From Fig. 4C, it could be seen clearly that NiO was tightly dispersed on the surface of CdS. The pore volume decreased a little as shown in Table 1, which was might because some NiO nanoparticles were incorporated in the pore of CdS. It is interesting to note that the content of nickels (detected by ICP and EDS) deposited on CdS under neutral solution was more than ones that deposited under alkaline solution as shown in Table 1, which also could be inferred from UV-vis (Fig. 1) and XPS (Fig. 3) results.

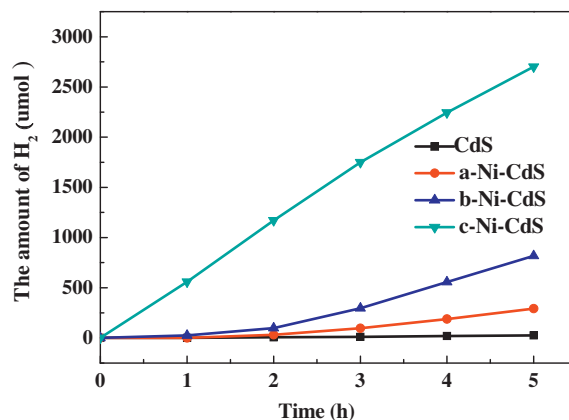
The nickel oxides deposited on CdS via in situ photodeposition in different solution are so different may caused by following reasons: (1) Nickel or its oxides can be react with HCl, so they are difficult to deposit on CdS under acid solution. (2) In neutral solution, nickel oxides are deposited on CdS in the form of Ni₂O₃ as following equation:



So Ni₂O₃ can only deposited at the active sites of CdS, and Ni₂O₃ species can act as electron traps and facilitate the charge separation, which can accelerate Ni₂O₃ photodeposition [18,22]. Therefore, Ni₂O₃ deposited and gathered on the surface of CdS particles as shown in Fig. 4B. (3) When NaOH was added in the solution, Ni²⁺ quickly dispersed on CdS in the form of Ni(OH)₂, then, the Ni²⁺ in Ni(OH)₂ was reduced to Ni by the photo-generated electrons from CdS. However, the metal nickel nanoparticles were not stable and could be easily oxidized into NiO [5]. Therefore, NiO nanoparticles dispersed highly on the surface of CdS as shown in Fig. 4C and D.

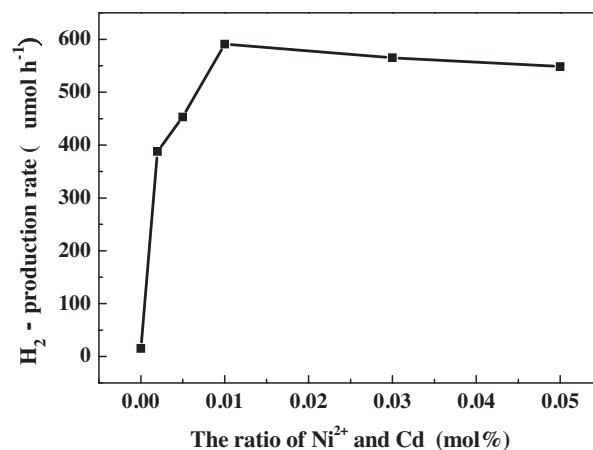
3.2. Photocatalytic performance of CdS loaded nickels via in situ photodeposition under different solution

The photocatalytic activities for H₂ evolution over different samples were shown as in Fig. 5. CdS alone showed very low photocatalytic activity of 5.0 μmol h⁻¹ because of the rapid recombination of photogenerated charges and a lack of H₂ evolution sites. After in situ photodeposition of nickel oxides under different solution, the H₂ production rates were improved apparently, which indicated that nickel or/and its oxides were excellent cocatalysts for photocatalytic H₂ production. The hydrogen evolution rate increased to 58.6, 261.4, 540.2 μmol h⁻¹ under acid, neutral and alkaline photodeposition solution, respectively.

**Fig. 5.** Comparison of the photocatalytic H₂-production activity of CdS, a-Ni-CdS, b-Ni-CdS and c-Ni-CdS under visible light irradiation.

The influence of the amount of nickel ion on the H₂ evolution rate under NaOH solution was shown as in Fig. 6. After a small amount of Ni²⁺ was added in the photodeposition solution (the mole ratio of Ni²⁺ and Cd was 0.002), the H₂ evolution rate increased to 387.3 μmol h⁻¹. Further increasing the amount of Ni²⁺ in the solution (the mole ratio of Ni²⁺ and Cd was 0.01) led to the highest H₂ evolution rate of 590.8 μmol h⁻¹ with a quantum efficiency of 8.6% at 400 nm when methanol was as sacrificial agent. Further increasing the content of Ni²⁺ ion in the photodeposition solution led to a slight drop of the H₂ evolution rate, probably because of a shielding effect of the NiO deposited on CdS.

Besides the influence of speciation, morphology and content of nickel oxides deposited on CdS, the added NaOH could also contribute to the enhancement of the photocatalytic H₂ evolution activity. The H₂ evolution rate increased to 15.1 μmol h⁻¹ when 0.5 g NaOH was added to the solution, while CdS alone showed a

**Fig. 6.** Influence of nickel concentration on H₂ evolution over CdS catalysts loaded nickel oxides via in situ photodeposition suspended in NaOH solution.

low activity of $5.0 \mu\text{mol h}^{-1}$. Similar phenomena had also found by Kudo et al., who reported that NaOH could enhance the photocatalytic activities of TiO_2 loaded with NiO [24]. It had also been reported that some other basic salts such as carbonate could enhance the photocatalytic H_2 evolution activities of $\text{NiO}_x/\text{TiO}_2$ photocatalysts [25]. As known, CH_3OH , as sacrificial agent, can react with holes produced from CdS after irradiation, which can retard photo corrosion. And electrons can be transferred to the cocatalysts NiO quickly and reduce H_2O into H_2 . When NaOH was added to the solution, alkaline environment might be benefit for holes oxidizing CH_3OH . Therefore, the holes and electrons could be separated more efficiently and the photocatalytic H_2 evolution activity was improved apparently.

Thus, the high hydrogen evolution activity of CdS loaded with nickel oxides under alkaline solution is due to the high and tight dispersion of nickel oxides on CdS and better holes transfer. It is indicated from the experiments that nickels were difficult to be coated on CdS in acid solution. However, in neutral solution, Ni_2O_3 , as electron traps and facilitated the charge separation [18], could deposit and gather on the surface of CdS, which improved its photocatalytic hydrogen production activity apparently.

4. Conclusions

The environment of deposition plays an important role in the photocatalytic H_2 evolution activities of CdS loaded nickels via in situ photodeposition. The photocatalytic H_2 evolution activity of CdS loaded with nickel oxides in neutral solution is higher than the one in acid solution while lower than the one in alkaline solution. This is because that nickel oxides are difficult to coat on CdS under acid solution. Ni_2O_3 can deposit and gather on the surface of CdS in neutral solution, which can be as electron traps and facilitate the charge separation for improving the photocatalytic hydrogen activity. The NaOH solution can enhance the photocatalytic H_2 evolution activity sharply (with a quantum efficiency of 8.6% at 400 nm when methanol was as sacrificial agent) because cocatalysts NiO disperse on CdS tightly and OH^- can accelerate holes transfer. The findings from this work are expected to offer insights on how to enhance the photocatalytic H_2 evolution activity by controlling cocatalysts deposition and photocatalysis environment.

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